Differential thermal analysis (DTA) and differential scanning calorimetry (DSC) as a method of material investigation

Diferenčna termična analiza (DTA) in diferenčna vrstična kalorimetrija (DSC) kot metoda za raziskavo materialov

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Abstract: Thermal analysis is used to establish thermodynamic properties which are essential for understanding the behavior of material under different heating and cooling rates, under inert, reduction or oxidation atmosphere or under different gas pressures. Thermal analysis comprises a group of techniques in which a physical property of a substance is measured to a controlled temperature program. In this paper only two methods are presented: differential thermal analysis (DTA) and differential scanning calorimetry (DSC). The results given from the DTA or DSC curves depend on the preparation of the material, and on the instrument sensitivity. The sensitivity is in close relation to the apparatuses design. Several types of DTA and DSC apparatuses are described as well as the use. New types of DSC devices are being developed which will have the capability of high heating / cooling rates and with shorter response time.

Izvleček: Termična analiza podaja termodinamske lastnosti materiala, ki so pomembne za razumevanje vedenja materiala pri različnih segrevalnih in ohlajevalnih hitrostih, bodisi v inertni, redukcijski ali oksidacijski atmosferi ali pri različnih tlakih. Termična analiza združuje skupino tehnik, kjer je preiskovan vzorec izpostavljen kontroliranemu temperaturnemu programu. V tem članku sta predstavljeni le dve metodi: diferenčna termična analiza (DTA) in simultana termična analiza (STA). Rezultati so bolj ali manj odvisni od priprave

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vzorca in nazadnje tudi od občutljivosti naprave. Občutljivost merjenja je v ozki povezavi s konstrukcijo naprave. V tem članku so opisani različni tipi DTA- in DSC-naprav ter možna uporaba le-teh. Novi tipi DSC-naprav se razvijajo v smeri visokih hitrostih segrevanja in ohlajevanja z majhnimi odzivnimi časi.

Key words: DTA, DSC, thermal analysis
Ključne besede: DTA, DSC, termična analiza

Introduction

Thermal analysis (TA)

Thermal analysis comprises a group of techniques where the properties of material are studied as they change with temperature. To determine the thermo-physical properties several methods are commonly used: differential thermal analysis (DTA), differential scanning calorimetry (DSC), thermogravimetric analysis (TGA), dilatometry (DIL), evolved gas analysis (EGA), dynamic mechanical analysis (DMA), dielectric analyse (DEA) etc. In metallurgy, material science, pharmacy and food industry the main application of the DTA and DSC is used for studying phase transition under different atmospheric influences, temperatures and heating / cooling rates. Common laboratory equipment has a combination of two thermal analysis techniques. Most common is the simultaneous thermal analysis (STA) apparatus as the combination of thermogravimetric analysis (TGA) and differential thermal analysis (DSC).

Definitions of DTA and STA methods

The two methods (DTA and DSC) are defined as followed:

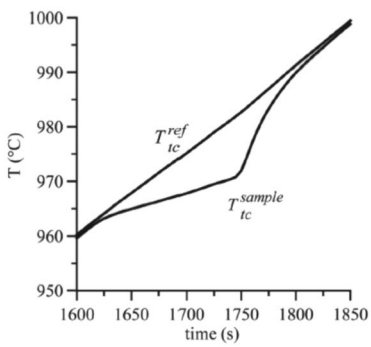
Differential thermal analysis (DTA): Thermal analysis using a reference. The sample and the reference material (sample) are heated in one furnace. The difference of the sample temperature and the reference material temperature is recorded during programmed heating and cooling cycles.[1]

Differential Scanning Calorimetry (DSC): Differential Scanning Calorimetry (DSC) measures the change of the difference in the heat flow rate to the material (sample) and to a reference material while they are subjected to a controlled temperature program.[1]

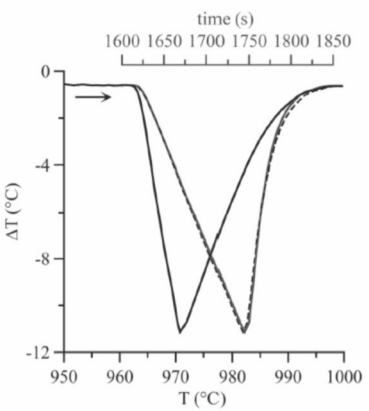
Like differential thermal analysis (DTA), differential scanning (DSC) is also an alternative technique for determining the temperatures of the phase transitions like melting point, solidification onset, re-crystallization onset, evaporation temperature etc. With differential thermal analysis DTA, which

is an older technique than differential scanning calorimetry, the result is a DTA curve (Figure 1b). DTA curve is a curve of temperature difference between the sample material and the reference material versus temperature or time. The result of DSC is a curve of heat flux versus time or temperature and is therefore used also for determination of the enthalpy, specific heat (c_p) etc.[2] Heat flow rate signal (DSC signal) is internally calculated from the temperature difference between the sample material and the reference material. The important difference between DSC and DTA equipment is that the latter is mostly used for the qualitative measurements and it is more robust because of less sensitive materials used for sample holders, heat conduction path etc. The sample holder in the DTA apparatus is much cheaper than the sample holder in the DSC apparatus and is recommended for the investigation of materials with an unknown relation to contamination between the crucible and the sample holders. Sample holders are commonly made of Al_2O_3 with integrated thermocouples. In the case of DSC the technique is more sensitive and allows several modifications which make it possible to measure the thermal conductivity, evolved gas analysis, thermogravimetry and activation energy for the grain growth, precipitation, etc. Sampler holders are commonly made of platinum.

It is typical for the DTA that the sample and the reference material are under identical temperature regime. This is not true in the case of the DSC method. In this case the method with two furnaces can also be used (Power compensation DSC).

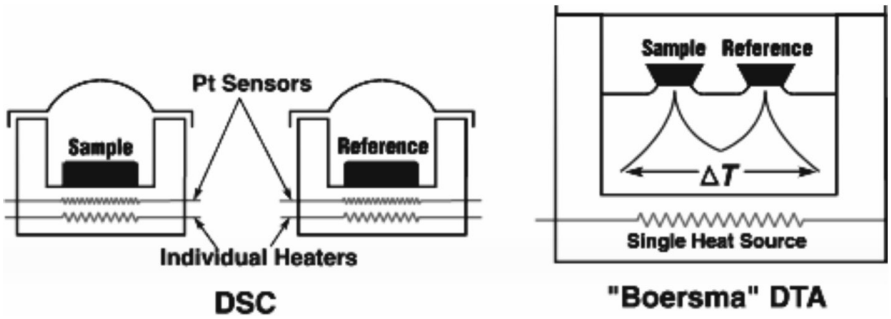


(a)



(b)

Figure 1. DTA heating curve for pure Ag (10 K/min): the sample and the reference temperature (a) and DTA signal as dependence of time and temperature (b)



(a) (b)

Figure 2. Shematic layout of the DSC apparatus: PC-DSC (a) and quantitative (Boersma) DTA or HF-DSC[3] (b)

Two basic types of Differential Scanning Calorimetry (DSC) must be distinguished: the heat flux DSC and the power compensation DSC. Sometimes a third basic type is also distinguished called the Hyper DSC which is an apparatus for rapid solidification based on power compensation DSC. Figure 2 represents both basic types of DSC apparatuses.

The power compensation DSC or PC – DSC has an individual heater for each chamber (figure 2 a). In the case of the heat flux or HF – DSC, both the sample and the reference material are inside the same furnace. The HF - DSC is also known as a type of Boersma DTA. The PC – DSC is more effective because the time constants (characteristic response time) are shorter. The characteristics of each device can be described with three characteristic times:

$$t_{S,C} = m_C C_p^C / h_{S,C} A_{S,C} \quad (1)$$

$$t_{W,C} = m_C C_p^C / h_{W,C} A_{W,C} \quad (2)$$

$$t_{S,C} = m_T C_p^T / h_{T,C} A_{T,C} \quad (3)$$

Where:

$t_{S,C}$, $t_{W,C,}$ $t_{T,C}$ – characteristic times for the heat flow between the metal sample and the crucible cup, the furnace wall and the crucible cup, the thermocouple and the crucible cup

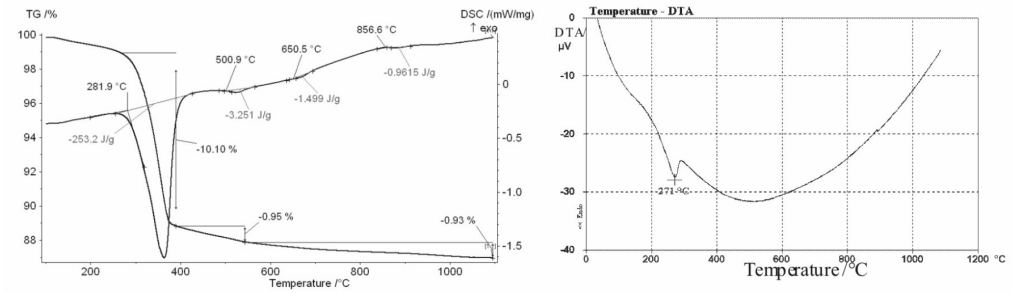
$h_{T,C}A_{T,C}$, $h_{W,C}A_{W,C}$, $h_{S,C}A_{S,C}$ - products of heat transfer coefficient and areas of heat flow

m_C, m_T – mass of the crucible (C) and the thermocouple (T)

C_P^c, C_P^t - heat capacity (J/K)

DIFFERENTIAL THERMAL ANALYSIS (DTA)

Differential thermal analysis (DTA) was constructed soon after the development of the thermocouple (1887, Le



(a) (b)

Figure 3. DSC/TG heating curve (a) and DTA heating curve for the limonite (b)

Chatelier). It was made for the examination of different materials. Most of the research efforts were made on clay and carbonate materials. The limitation in the DTA apparatuses is its sensitivity. This is shown by the next mineral called limonite. The difference in the DTA and DSC heating curves are represented in figure 3.

In figure 3 a at least three separate decompositions were determined by the DSC and TG curve. The DTA curve showed only one because the quantity of the released heat was too small to be detected.

Nevertheless, the DTA curves can record the transformations where the heat is either absorbed or released (dehydration, decarbonation, burning of materials, ordering etc.). DTA is helpful for better understanding of given results by x-ray diffraction, chemical analysis and microscopy.[4]

The most important advantages of the DTA are its simplicity and a possibility to create different experimental conditions (high pressure or vacuum).

DTA can also be used for quantitative measurements (enthalpy measurements). The DTA has advantages over DSC because it allows simultaneous recording of changes in the sample mass, while DSC requires a constant mass during the enthalpy change measurement. DSC directly measures the energy change of a sample while DTA measures the temperature difference between the reference and the sample, which is converted to enthalpy change (ΔH) through conversion factors (which are difficult to determine). The enthalpy calculation with DTA is done using the mass difference baseline method. An inert sample must be used (e.g. sapphire) for estimating the conversion factors K1 and K2. The relation for estimating the conversion

factors is represented with equation 4:[5]

$$\frac{dH}{dt} = K1K2\frac{(DTA1 - DTA2)}{(ms,1 - ms,2)} \quad (4)$$

Where;
$K1$ – determined by the heat transfer from the furnace to the sample – depends on the heat transfer coefficient α_s (by fixed operation conditions it is estimated to be temperature independent)
$K2$ – apparatus related parameter (temperature dependent)
$DTA1 - DTA2$ – the area between two DTA curves
$m_s,1$; $m_s,2$ – mass of the inert sample
dH/dt – specific heat capacity of the sample (sapphire)

Because the DTA allows the sample mass loss during the measurement, it is considered useful for the materials with intensive decomposition (elastomers, exothermic materials etc.). As already discussed the classical DTA apparatus, because of inexpensive materials (main elements are mostly made of ceramics) used, more volatile and reactive systems can be analyzed. Temperature regions are commonly up to 1500 °C with heating and cooling rates up to 50 K/min. Crucibles are mostly made of Al_2O_3, platinum or graphite with 85 µL volumes or less. Different atmosphere can be used. When decomposition of clays or other decompounding samples is analyzed, the measurements are often done under an oxidation atmosphere. High performance modular DTA are DTA systems with widest temperature range –150–2400 °C. Crucibles here are made of tungsten or graphite. It is important to use inert atmosphere to prevent degradation of the crucibles.

Micro differential thermal analysis (µ-DTA)

Just like classical DTA, the DSC also has the same disadvantages, especially when bigger masses are used. With heavier loads the responding time is longer and the interpretation of such a curve is more difficult. A new device called µ-DTA was developed, presented in figure 4.[6]

The sample masses are around 50 µg. Minimum load depends on the system itself and on the type of the sample. Literature (Senesac, Yi etc. [7]) also describes a load of 600×10^{-12} g of explosive adsorbed molecules with characteristic responce time 50 ms which is extremely low and makes this system special than the others.[7]

The system consists of two micro hotplates with two integrated heaters (figure 4) to ensure a homogenous temperature distribution. The wetting of the membrane surface is the most important characteristics to ensure an optimal heat transfer. Integrated TiW thermistors are used for the temperature measurement and are located under the specimen. One

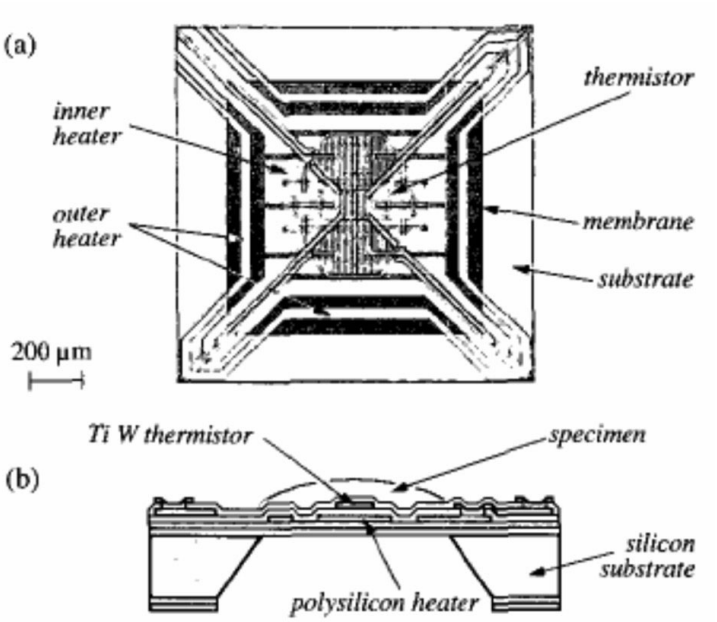


Figure 4. Schematic representation of µ-DTA: optical micrograph of a membrane with inner and outer polysilicon heaters and central TiW thermistor (a) and schematic cross section of the membrane with melted specimen (b) [6]

of the membranes is used as a reference. [6] A big disadvantage of this method although that it is not possible to process metals because of high specific surface tension (small or no wetting of the membrane), is high oxidation process caused by high specific surface of the sample. For this system it is necessary not to use oxidising atmosphere. Many apparatuses are used for differential thermal analysis of frozen food systems, especially at lower temperatures (down to –180 °C). [8] Classical temperature ranges are between –45 °C and 120 °C (maximum up to 200 °C). Heating cooling rates are up to 2 K/min which is much slower than at the common DTA apparatuses. Also the maximal pressure for this type of design is much lower than at the classic DTA apparatus which is higher than 1 bar.

High pressure differential thermal analysis HP - DTA

Excessive evaporation can reduce the sample mass and change the chemical composition which leads to incorrect measurement of the characteristic temperatures. For studying the thermodynamics of different systems by using different gas pressure, the (high pressure differential scanning calorimetry) HP-DTA apparatuses were designed. Multi component systems can decompose if required gas pressure (normally by using argon) is not as close as possible to the synthesis conditions. Pressure range

for the HP-DTA are often wide up to several hundreds bars, but with a narrow temperature range (–150 °C to 600 °C). Heating and cooling rates are normally around 20 K/min. [1, 9] New apparatuses have heating and cooling rates up to 50 K/min at maximum pressure 150 bar. For understanding phase transitions during high pressure, HP DSC apparatuses were designed with a higher sensitivity.[10] HP-DSC experiments can be performed using 2–4 mg samples sealed in aluminium pans which have better response (as platinum, graphit, gold etc.). Cylindrical tin pans are used for most HP-DTA experiments. The dependence of the melting temperature to the pressure is described by the Clausius - Clapeyron equation:

$$\frac{dP}{dTm} = \frac{\Delta Hm}{Tm \cdot \Delta Vm} \tag{5}$$

Where:
ΔH_m – melting enthalpy
ΔV_m – volume difference between solid and liquid
dP – pressure difference
dT_m – Difference in melting temperatures

Equation 5 states that the melting temperature will change with changing the pressure, which can be determined from the DTA curve. Calculation of the change in the melting enthalpy can be calculated from equation 5. Investigation of the sample can be done under atmospheric pressure or by the hydrostatic pressure were different oils are used as pressure transmitting medium. The electronic pressure control device as well as exact regulation of the purge gas (oil) flow is the main feature for outstanding accuracy and reproducibility of the measurements.

Differential Scanning Calorimetry (DSC)

DSC measures the rate of the heat flow to the sample and the reference. DSC is useful in making the same measurements as DTA and has the capability to measure heat capacities and thermal conductivity. Three basic types of DSC must be distinguished:

- heat flux DSC
- power compensation DSC
- Hyper DSC

The primary measurement signal for all three types is a temperature difference; it determines the intensity of the exchange of the heat between the furnace and the sample-reference part. The resulting heat flow rate Φ is proportional to the temperature difference. In the case of power compensation DSC, the apparatus consists of two identical micro-furnaces, one for the sample and the other for the reference. Both furnaces are separately heated; the sample furnace is heated with a temperature – time program, while the reference furnace tries

to follow this program. This includes increment-decrement of the temperature in the reference furnace, when a reaction takes place. In this case the compensating heating power is measured which is actually the heat flow difference.[12]

One of the problems in measuring the heat flow signal is the artefact, which is related to the instrumentation.[11] When a base line is run, one sees a start-up hook, offset, slope and curvature. An ideal baseline would be flat and without any artefacts. Base line artefacts are inherent in the design and manufacture of DSC instrumentation. Typical artefacts are related to the: crucible moving, sudden change in the heat flow rate between crucible and sensors, high frequency disturbance etc.

Heat Flux DSC

The most fundamental types are:

- The disk type measuring system
- The turret type measuring system
- The cylinder-type measuring system

The heat flux within the DSC takes place via a well defined heat conduction path with a low thermal resistance from furnace to the samples.[12] The disk type measuring system heat exchange takes place trough a disk which is solid sample support. Its features are high sensitivity and small sample volume. With turret type heat exchange takes place via small hollow cylinders which also serve as sample support. The turret type has higher sensitivity and faster response with large heating and cooling rates. Like with the disk type sample volume is small. In the case of the cylinder type measuring system the heat exchange takes place between the (big) cylindrical sample cavities and the furnace with a low thermal conductivity (termopile). Only low heating and cooling rates are possible. The sensitivity per unit volume is high even with a large sample volume. This system has a larger time constant than the first two measuring systems.

The disk type measuring system – Heat flux DSC

Figure 5 represents the Disk type DSC. The disk is designed to act as a sample support and the heat exchange measurement. The main heat flow from the furnace passes symmetrically trough the disk with a medium thermal conductivity; this is its main characteristic.[1] In some cases the disks are made with combination of metal (e.g. platinum) and covered with ceramics.

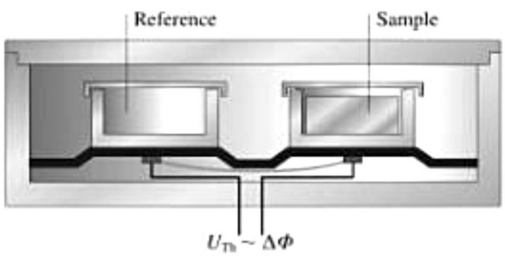


Figure 5. Schematic presentation of the heat flux DSC with a disk type measuring system[12]

In the heat flux DSC the connecting metal strip is often used as a sensor to obtain the temperature difference by measuring the voltage. The heat exchange from the furnace to the sample is limited and it allows only medium heating and cooling rates. Modification of the disk type of DSC is very common. One is HF-DSC with a triple measuring system. With three separate locations the measurement of specific heat is measured with just one run.[1] In the classic HF-DSC device three measurements must be made (with an empty crucible, with a sapphire or a known inert sample and with the investigated sample). Another modification is high pressure HF-DSC, which is used to determine vapour pressures and heats of evaporation.[1]

Typical crucible materials for the DSC apparatuses are made of Al, Al_2O_3, graphite, Y_2O_3, Pt/Rh with Al_2O_3 inside the crucible, gold etc. Different atmospheres can be used. Common heating or cooling rate is 10 K/min. Typical time constant is between 3 s and 10 s which is much longer than with μ-DTA. For special applications (measurement under high pressure) the crucibles are made of stainless steel with a golden cover or titan with 0.19 mL volume.

The Cylinder measuring system – Heat flux DSC

The heat flux DSC operating on Calvet principle is using a cylinder type measuring system by two sintered alumina cylinders set parallel and symmetrical in the heating furnace. The crucible used here is produced from stainless steel.[13] The HF-DSC with the cylinder measuring system is appropriate for large samples. In the case of inhomogeneous alloys large samples are needed because of local differences in the chemical composition. In comparison to micro DTA the characteristic time is much larger, which can cause problems in determining temperatures of small phases with small quantities. In the figure 6, the heat which is conducted to the sample via a large number of thermocouples, changing the sample temperature is shown

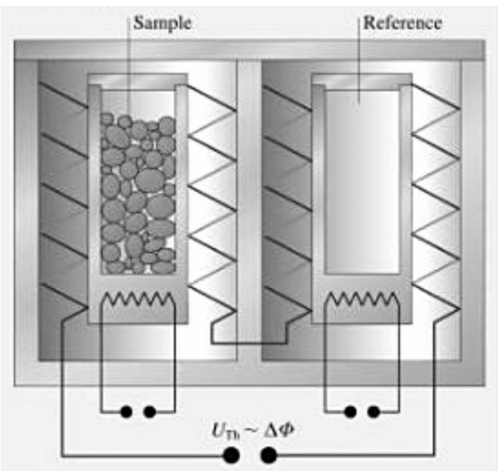


Figure 6. The heat flux DSC with a cylinder-type measuring system (Calvet)[12]

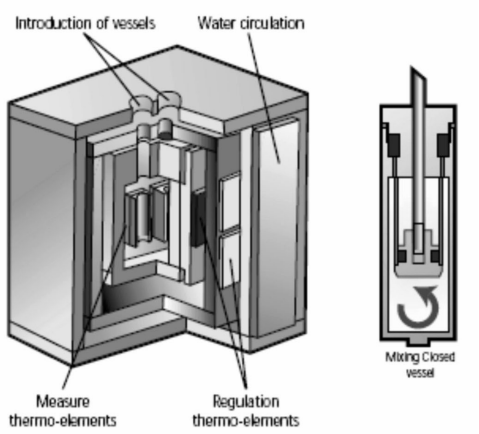
The temperature difference ΔT of both sample containers is generated by differential connection to both thermo-

couples. The problem can appear if the height of a sample is not sufficient enough. Compared with the other apparatuses, the cylinder type has a much larger volume and therefore a longer time constant which can be as long as 40 min. Nevertheless a measurement can also be done in a wide temperature range (–196–1500 °C).[1] Sample volumes of the crucibles are approximately 10 mL larger than those used for classical disk type measuring system. Larger crucibles (100 cm^3) are also used for investigation in biology. These DSC's can usually have the maximum heating rate up to 1 K/min.

Micro differential DSC – modified HF DSC

This method is a combination of an isothermal calorimeter and a HF-DSC mode device. In an isothermal calorimeter, the heat generated by the sample, flows trough the thermal resistance into a water jacket (Figure 7). The temperature difference across the thermal resistance is measured.[3]

Micro DSC has the same ability to measure the thermal properties as an ordinary DSC device. One of the advantages is a very high sensitivity but on the other hand the temperature range is very narrow (–20 °C to ≈120 °C). With this type of device it is ideal to study crystallisation because the cooling and heating rates can be even lower than 0.001 °C/min (with a response time of few seconds) and is also suitable to determine phase transitions like intermediate phases between solid and liquid in Liquid crystals.[15]



(a) (b)

Figure 7. The heat flux Micro differential DSC: the setup of the device (a) and mixing vessel for determination of the mixture heat (b)

Different vessels are usually needed for the measurement. A special vessel is used for studying the amounts of heat mixture between two liquids or between a liquid and a solid.

The energy of mixing is absorbed or released heat, where the changes in the volume (V) under pressure (p) are negligible ($H = U + pV$). It represents the difference in internal energy (U) before and after mixing.[16]

The mixing vessel is represented in figure 7b. The vessels are made of Hastel-

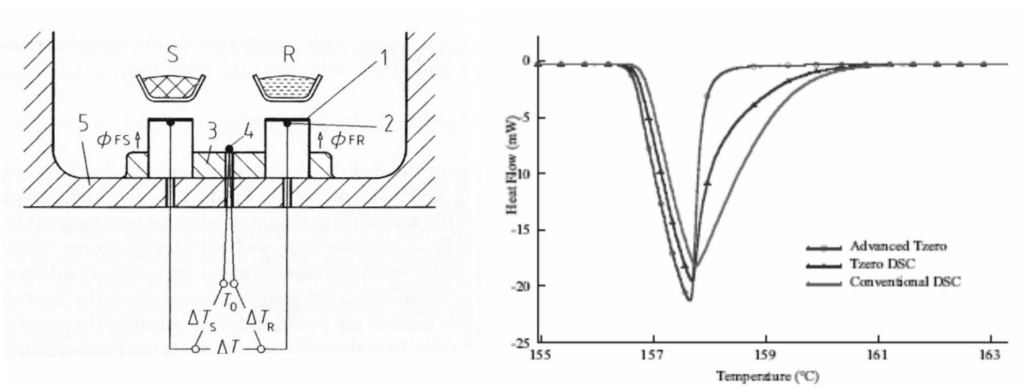
loy C276 and their volume is 1 cm^3. The measurement of adsorption heat can also be done. With modification this type of DSC can be made into a high pressure micro DSC (HP micro DSC) with maximum pressure of 20 bar. The classical micro DSC like micro DTA apparatuses is applied for 1bar. Modified HF-DSC is a powerful technique, but with existing technology it is limited to heating rates of no more than 5 K/min. As a response to that disability a new Tzero technology was developed with a turret type measuring system.

The turret-type measuring system – HF DSC

Small hollow cylinders are used for sample support and for the heat exchange. The turret type of the HF DSC is represented in figure 8. The turret measuring system is ideal for determining the purity of metals.

This type of the HF-DSC is still one of the options of possible leading DSCs on the market in the future. The advantage of the turret system is in the heat transfer from the jacket to the sample, because it goes through a thin-walled cylinder. This way a very short heat conducting path is achieved. The system is very small thus the characteristic time is very short. No interference between the sample and the reference is present. The turret type is special because of a third thermocouple which measures the thermal inertia. This is a so-called Tzero DSC technology.[1]

The DSC causes the distortion in the DSC curves (in the true shape of the peak) because of a: sample-reference side asymmetry, thermal resistance and thermal capacitance gap of the cell, pan. The temperature reference sensor (figure 9) allows the detection of these effects and they are compensated with an original DSC curve.



(a) (b)

Figure 8. The turret type measuring system HF-DSC [1] (a) and effect by melting indium[1, 18] (b) specimen[6]

The result is the real (actual) DSC curve (figure 8 b) shown as a dependence of the sample and not of the instrument. [18] Crucibles for this type of DSC (also known as Tzero DSC) apparatuses are made of similar or same material as for the classical DSC apparatuses. This system is relatively new and is due to good results a good competition to the, so far, predominant power compensation DSC and also micro-DSC. New Tzero design is able to detect the glass transition temperature (Tg) of polypropylene, normally not detectable by any current DSC.[19] Heating rates are up to 200 K/min. Theoretically a time constant in this case should be zero but is close to values of the micro DSC and lower.

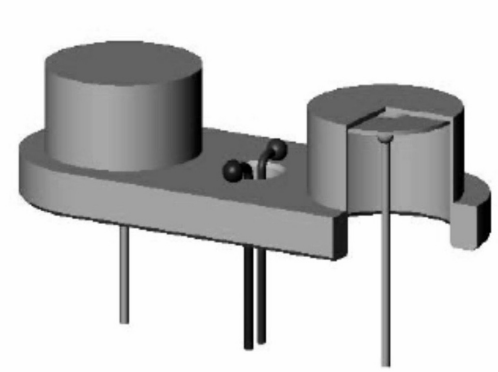


Figure 9. Position of the reference sensor: Tzero™ sensor[17]

Power Compensation DSC

Sample and reference are each held in a separate, self contained calorimeter with its own heater (Figure 10).

The advantage of the PC DSC over the HF-DSC is a very light individual furnace. The power compensated furnaces weigh 1 g. The furnaces for HF DSC weigh up to 200 g.[21] The effect of a low mass furnace is an extremely short responding time. The heating and cooling rates can be up to 500 °C/min. When a reaction appears (exothermal or endothermal) the energy is accumulated or released to compensate the

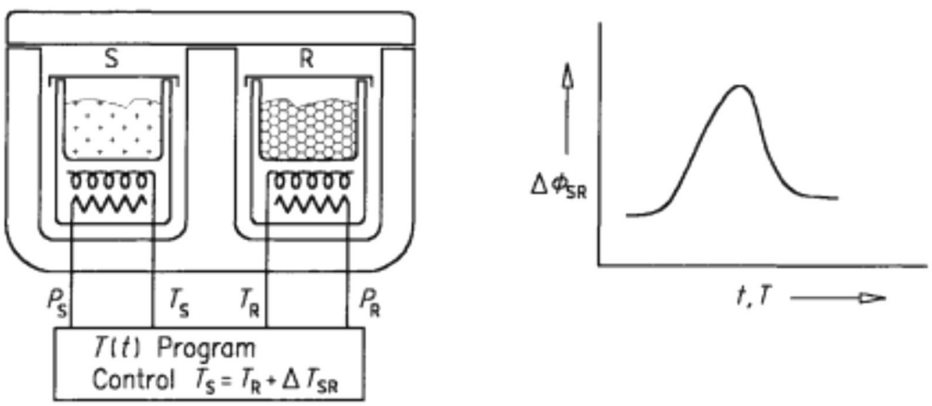


Figure 10. Power compensating DSC (Perkin – Elmer Instruments)[20]

energy change in both furnaces. The power required to maintain the system in equilibrium is proportional to the energy changes occurring in the sample. [1, 21]

All PC DSC are in basic principles the same. But special PC DSC has also been presented in the past. One of them is Photo DSC where direct measurements of radiation flow occur under a light source. This way the degradation of material can also be observed. The maximum heating rate for not modified PC DSC is up to 500 K/min and the maximum cooling rate is up to 400 K/min. Temperature range of measurement is up to 400 °C with time constant of only 1.5 s or lower. Sample masses are around 20 mg. Crucibles of different volumes (lower than several ten cubic millimetres) are made mostly of aluminium.

Hyper DSC

The high resolution of PC-DSC or new type of power compensating DSC provides the best results for an analysis of melting and crystallisation of metals or detection of glass transition temperature (T_g) in medications. Fast scan DSC has the ability to perform valid heat flow measurements with fast linear controlled rates (up to 500 K/min) especially by cooling, where the rates are higher than with the classical PC DSC. Standard DSC operates under 10 K/min. The benefits of such devices are increased sensitivity at higher rates (which enables a better study of the kinetics in the process), suppression of undesired transformation like solid – solid transformation etc. [22] It has a great sensitivity also at a heating rate of 500 K/min with 1 mg of sample material. This technique is specially proper for the pharmaceutics industry for testing medicaments at different temperatures where fast heating rates are necessary to avoid other unwanted reactions etc.

CONCLUSIONS

Several types of the DSC and also DTA devices have been developed in order to achieve as good sensitivity as possible. This depends on the type of the sample or material and its preparation. In some cases the sensitivity can be improved by using smaller samples, if and when it is possible. When this is not possible, the sensitivity mostly depends on the mechanical parts which are used as a thermal path from the furnace to the sample and from the sample to the thermocouples or other detectors. For minimal mechanical effect, different types of measurement devices are constructed. Best results are expected to be achieved by the so called PC DSC apparatuses and hyper DSC.

References

[1] Höhne, G. W. H., Hemminger, W. F., Flammersheim, H. J. (2003): Differential Scanning Calorimetry; Springer Verlag Heidelberg, New York.

[2] Boettinger, W. J., Kattner, U. R., Moon, K. W. (2006): DTA and Heat-flux DSC Measurements of Alloy Melting and Freezing; Metallurgy Division, Material Science and Engineering Laboratory, National Institute of Standards and Technology.

[3] http://personal.cityu.edu.hk/~bhtan/PerkinElmerThermal.ppt

[4] Richards A. Rowland: Differential Thermal Analysis of clays and carbonates

[5] Yang, J., Roy, C. (199): Using DTA to quantitatively determine enthalpy change over a wide temperature range by the mass-difference baseline method; Thermocimica Acta 333; pp. 131–140.

[6] Patrick Ruther, Markus Herrscher, Oliver Paul; A micro differential thermal analysis (μDTA) system; IEEE (2004); pp. 165–168.

[7] L. R. Senesac, D. Yi, A. Greve, J. H. Hales, Z. J. Davis, D. M. Nicholson, A. Boisen, T. Thundat; Micro-differential thermal analysis detection of absorbed explosive molecules using microfabricated bridges; Rev. Sci. Instrum.; 80; 2009

[8] L. G. Parducci, R. B. Duckworth (2007): International Journal of Food Science and Technology, Vol. 7, No. 4; pp. 423–430.

[9] S. L. Johnson, S. Guggenheim & A. F. K. van Gross; Thermal stability of halloysite by high-pressure differential thermal analysis; Clays and Clay Minerals,Vol. 38, No. 5, pp. 477–484,1990

[10] S. Zhu, S. Bulut, A. Le Bail & H. S. Ramaswamy;High-pressure differential scanning calorimetry (DSC): equipment and technique validation using water-ice phase transition data; Journal of Food Process Engineering:vol.27,5; pp. 359–376;2005

[11] Robert L. Danley; New heat flux DSC measurement technique; Thermochimica acta 395 (2003); pp. 201–208.

[12] Czichos, Saito, Smith; Materials Measurement Methods; Springer 2006; pp. 411–413.

[13] C. M. Santos, M. M. S. Ribeiro, M. J. V. Lourence, F. J. V. Santos & C. A. Nieto de Costro; Recent Advances on TG-DSC Accurate measurement;17th Europian Conference on thermophysical Properties, Bratislava, Slovakia, 2005

[14] L. L. Van Zyl; An isothermal calorimeter with sample temperature control. J. Sci. Instr. Vol. 41; 1964; pp.197–202

[15] http://www.ices.a-star.edu.sg/ices/documents/MicroDSC.pdf

[16] Vasilij Gontarev; Termodinamika materialov; Naravoslovnotehniška

fakulteta, Oddelek za materiale in metalurgijo, 2004

[17] http://www.tainstruments.co.jp/application/pdf/Thermal_Library/Applications_Briefs/TA295a.PDF

[18] Cassel Bruce; How Tzero™ Technology Improves DSC performens Part 11. Peak Shape and Resolution; TA278; pp. 1–3

[19] http://www.tainstruments.com/library_download.aspx?file=TA271.pdf

[20] Michael E. Brown; Handbook of Thermal Analysis and Calorimetry: Principles and practice; Elsevier, 1998

[21] W. J. Sichina; Benefits and applications of the Power Compensated Pyris 1 DSC; PE Tech-51 Thermal Analysis; 2000

[22] Pijpers, M. F. J., Mathot, V. B. F. (2008): Optimisation of instrument response and resolution of standard – and high speed power compensation DSC; Journal of Thermal Analysis and Calorimetry; Vol. 93; pp. 319–327.